

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

BRNO UNIVERSITY OF TECHNOLOGY

FAKULTA CHEMICKÁ
ÚSTAV FYZIKÁLNÍ A SPOTŘEBNÍ CHEMIE

FACULTY OF CHEMISTRY
INSTITUTE OF PHYSICAL AND APPLIED CHEMISTRY

PREPARATION OF STUCTURED THIN LAYERS OF TITANIUM
DIOXIDE

BAKALÁŘSKÁ PRÁCE
BACHELOR'S THESIS

AUTOR PRÁCE
AUTHOR

Ing. MAGDALENA LUKEŠOVÁ

BRNO 2009



VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
BRNO UNIVERSITY OF TECHNOLOGY



FAKULTA CHEMICKÁ
ÚSTAV FYZIKÁLNÍ A SPOTŘEBNÍ CHEMIE
FACULTY OF CHEMISTRY
INSTITUTE OF PHYSICAL AND APPLIED CHEMISTRY

PREPARATION OF STRUCTURED THIN LAYERS OF TITANIUM DIOXIDE

PŘÍPRAVA STRUKTUROVANÝCH TENKÝCH VRSTEV OXIDU TITANIČITÉHO

BAKALÁŘSKÁ PRÁCE
BACHELOR'S THESIS

AUTOR PRÁCE
AUTHOR

Ing. MAGDALENA LUKEŠOVÁ

VEDOUCÍ PRÁCE
SUPERVISOR

doc. Ing. MICHAL VESELÝ, CSc.

BRNO 2009



Vysoké učení technické v Brně
Fakulta chemická
Purkyňova 464/118, 61200 Brno 12

Zadání bakalářské práce

Číslo bakalářské práce:	FCH-BAK0262/2008	Akademický rok: 2008/2009
Ústav:	Ústav fyzikální a spotřební chemie	
Student(ka):	Ing. Magdalena Lukešová	
Studijní program:	Chemie a chemické technologie (B2801)	
Studijní obor:	Spotřební chemie (2806R002)	
Vedoucí bakalářské práce:	doc. Ing. Michal Veselý, CSc.	
Konzultanti bakalářské práce:		

Název bakalářské práce:

Příprava strukturovaných tenkých vrstev oxidu titaničitého

Zadání bakalářské práce:

1. Prostudujte metody přípravy mezoporézních a porézních vrstev oxidu titaničitého.
2. Z literárních zdrojů studujte vztah mezi strukturou tenké vrstvy oxidu titaničitého a jeho fotokatalytickými vlastnostmi.
3. Připravte mezoporézní tenké vrstvy oxidu titaničitého mikropiezo depozicí.

Termín odevzdání bakalářské práce: 29.5.2009

Bakalářská práce se odevzdává ve třech exemplářích na sekretariát ústavu a v elektronické formě vedoucímu bakalářské práce. Toto zadání je přílohou bakalářské práce.

Ing. Magdalena Lukešová
Student(ka)

doc. Ing. Michal Veselý, CSc.
Vedoucí práce

doc. Ing. Miloslav Pekař, CSc.
Ředitel ústavu

V Brně, dne 1.12.2008

doc. Ing. Jaromír Havlica, DrSc.
Děkan fakulty

ABSTRAKT

Cílem práce bylo seznámit se s dostupnými zdroji popisujícími zkoumanou tematiku tenkých vrstev oxidu titaničitého. Na připravených tenkých filmech byla studována fotokatalytická aktivita a indukované hydrofilní vlastnosti. Transparentní filmy oxidu titaničitého byly připraveny na sodnovápenatém skle metodou sol-gel. Na přípravu TiO_2 solu byl použit tetraisopropoxid titaničitý (TTIP) jako prekurzor. Přidaný polyethylen glykol (PEG) sloužil jako strukturu-řídící složka, acetyl aceton zase ovlivňoval hydrolyzační a kondenzační reakce. Pro nanášení solu na skleněné destičky byla použita technika mikropiezo depozice. Na získaných filmech byla studována fotokatalytická aktivita prostřednictvím degradace 2,6-dichlorindofenolu (DCIP). Rychlost odbourávání DCIP byla vyjádřena pomocí formální rychlostní konstanty reakce prvního řádu. Měřením kontaktního úhlu byla zkoumána smáčecí schopnost vrstev. Filmy, které byly vystaveny ultrafialovému záření, se chovaly superhydrofilně.

ABSTRACT

The aim of this work is to prepare titanium dioxide thin films, to study their photocatalytic activity and photoinduced hydrophilic properties. Transparent titanium dioxide films were prepared on soda-lime glass support by sol-gel method using titanium(IV)isopropoxide. Piezoelectric deposition was involved as a coating technique. TiO_2 sol was synthesized with a structure-directing and pore generating agent, polyethylene glycol (PEG) and acetylacetone (AcAc) as a complexing agent to control the hydrolysis and condensation reactions. The TiO_2 films were active in the photooxidation of 2,6-dichloroindophenol as resulted from the formal first order rate constant calculation. Also influence of ultraviolet light on the film hydrophilicity was studied by contact angle (CA) measurements. The prepared films became superhydrophilic after UV-light irradiation.

KLÍČOVÁ SLOVA

oxid titaničitý, tisk, fotokatalýza, mezoporézní vrstvy

KEY WORDS

titanium dioxide, print, photocatalysis, mesoporous layers

LUKEŠOVÁ, M. *Příprava strukturovaných tenkých vrstev oxidu titaničitého*. Brno: Vysoké učení technické v Brně, Fakulta chemická, 2009. 41 s. Vedoucí bakalářské práce doc. Ing. Michal Veselý, CSc.

DECLARATION

I declare that the diploma thesis has been worked out by myself and that all the quotations from the used literary sources are accurate and complete. The content of the diploma thesis is the property of the Faculty of Chemistry of Brno University of Technology and all commercial uses are allowed only if approved by both the supervisor and the dean of the Faculty of Chemistry, BUT.

.....
student's signature

Sincere acknowledgement belongs to doc. Ing. Michal Veselý, CSc. and the whole team from the photochemical laboratory.

I hear and I forget.
I see and I remember.
I do and I understand.

Confucius

CONTENTS

1	INTRODUCTION	8
2	THEORETICAL PART	9
2.1	Heterogeneous photocatalysis	9
2.2	Titanium dioxide	9
2.3	Titanium dioxide photocatalysis	11
2.3.1	Oxidation-reduction reactions	11
2.3.2	Characteristics of photocatalytic processes.....	12
2.3.3	Environmental semiconductor photocatalysis.....	13
2.3.4	Photo-induced superhydrophilicity	14
2.4	Immobilization of TiO ₂	15
2.4.1	Sol-gel method	15
2.5	Aspects effecting the TiO ₂ film structure.....	17
2.5.1	Effect of structure-directing agents	17
2.5.2	Effect of calcination temperature and calcination time.....	19
2.6	Piezoelectric deposition.....	20
2.7	Pre-treatment of soda-lime glass support	22
2.8	Kinetics of heterogeneous photocatalytic reactions	23
2.8.1	Langmuir-Hinshelwood	24
2.9	Chemical reactors	26
2.10	Instruments for TiO ₂ films characterization	26
2.10.1	UV/VIS spectrophotometry	26
2.10.2	Contact angle measurements	27
3	EXPERIMENTAL	28
3.1	Chemicals, devices and software.....	28
3.1.1	Chemicals	28
3.1.2	Devices	28
3.1.3	Software	28
3.2	Titanium dioxide film deposition	28
3.2.1	Substrate pretreatment.....	28
3.2.2	Sol synthesis	28
3.2.3	TiO ₂ film preparation	29
3.2.4	Photocatalytic activity of the TiO ₂ films.....	30
3.2.5	Contact angle measurement	33
4	RESULTS AND DISCUSSION	34
4.1	Photoinduced hydrophility of TiO ₂ thin films.....	34
4.2	Photocatalytic activity of TiO ₂ thin films.....	34

4.2.1	Calibration curve method	35
4.2.2	Photochemical degradation of 2,6-dichloroindophenol	35
5	CONCLUSION	37
6	REFERENCES	38
7	LIST OF ABBREVIATIONS.....	41

1 INTRODUCTION

Environmental pollution is one of the serious problems all around the world. Photocatalytic technology that is a widely studied topic could be effective in the environmental cleanup⁶. Titanium dioxide belongs to the group of popular and promising materials for photocatalytic applications, such as photocatalytic, photovoltaic, photoinduced superhydrophilical applications etc. According to the requirement of the application, titanium dioxide is needed to be modified. It is therefore very important to study the evolution of different physical and chemical properties of TiO₂, prepared by a suitable technique which is effective for controlled modification¹⁶.

Among the various techniques to prepare TiO₂ in immobilized form the most widely used one is the sol-gel method because of its ability to obtain films with tailored properties. TiO₂ film is prepared from alkoxide solution, where metal alkoxide precursor is hydrolyzed under controlled conditions to form an extensive three dimensional network. A possibility was found to improve the properties of titania thin films obtained by this way by means of suitable modification of the precursor with different agents. Added acetylacetone leads to slowing down of the sol-gel process and thus stabilizes the sol. Furthermore, modification by polyols such as polyethyleneglycol has a strong effect on gelation time, particle morphology, porosity, etc¹⁴.

High surface area mesostructured TiO₂ is used in photocatalysis for purification of water or air, for decomposing germs, viruses and dirt. The absorption characteristics allow titanium dioxide to absorb photons of UV light, producing reactive electron-hole pairs that can react with surrounding materials. The durability and stability of TiO₂ during such reactions make it an ideal material for any application where the material is to be used continuously without frequent replacement⁶.

The aim of this thesis was to summarize an actual aspect of the solved topic. This study also describes a method for preparing titanium dioxide thin films. In the next step photoinduced superhydrophilicity and photocatalysis were studied on TiO₂ coated soda-lime glass plates.

2 THEORETICAL PART

2.1 Heterogeneous photocatalysis

Heterogeneous photocatalysis (HP) involves photoreactions which occur at the surface of a catalyst. Basic principles of HP are as follows.

A semiconductor (SC) is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lowest empty band, called conduction band (CB), are separated by a bandgap. When a photon of energy higher or equal to the bandgap energy is absorbed by a SC particle, an electron from the VB is promoted to the CB with simultaneous generation of a hole (h^+) in the VB (Figure 1). The e_{CB}^- and h_{VB}^+ can recombine on the surface or in the bulk of the particle in few nanoseconds (energy is dissipated as heat) or can be trapped in surface states where they can react with donor or acceptor species adsorbed at the surface of the particle. Thereby, subsequently redox reactions can be initiated.

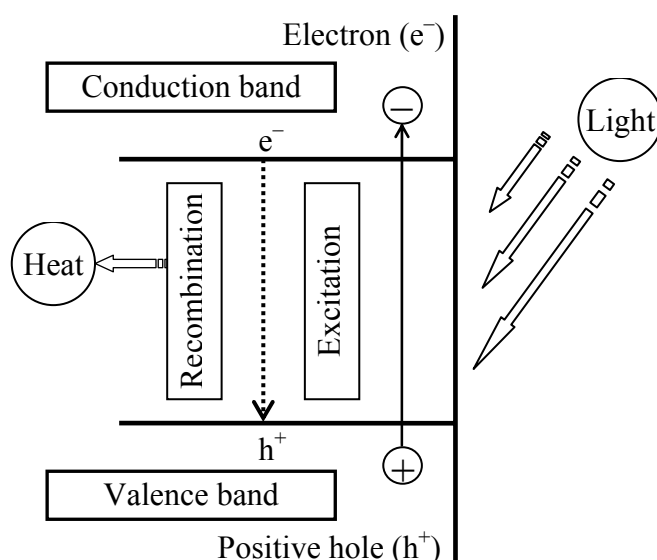


Figure 1 Simplified diagram of the heterogeneous photocatalytic processes on an illuminated semiconductor particle

Various factors can affect the photocatalytic reaction rate. For example, the pH of the solution determines the surface charge on the SC. Photocatalytic reactions originate in the interface, so adsorption processes seem to have a particular importance. The kinetics depends on the substrate concentration and also access of light, which promotes a faster electron-hole recombination. High temperatures generally lead to higher rates because they provoke a more frequent collision between the substrate and the SC. The presence of metal ions or inorganic anions in the solution is also of great importance¹.

2.2 Titanium dioxide

Titanium dioxide, more properly called titanium(IV) oxide, is a naturally existing semiconductor. It exists in three crystallographic forms – anatase, brookite and rutile (Figure 2), all with 6-coordinate titanium:

Rutile form – the most common form in tetragonal symmetry ($a = 4.594 \text{ \AA}$, $c = 2.958 \text{ \AA}$), exists both in nature and as produced commercially, it is a high pressure and temperature mineral found in igneous rocks².

Anatase form – tetragonal ($a = 3.793 \text{ \AA}$, $c = 9.51 \text{ \AA}$), crystals look like stretched out octahedrons, it is stable at low temperature, at about 915°C reverts to the rutile structure.

Brookite – titanium dioxide in an orthorhombic symmetry ($a = 5.456 \text{ \AA}$, $b = 9.182 \text{ \AA}$, $c = 5.143 \text{ \AA}$), it is also stable at low temperatures, reverts to rutile at about 750°C .

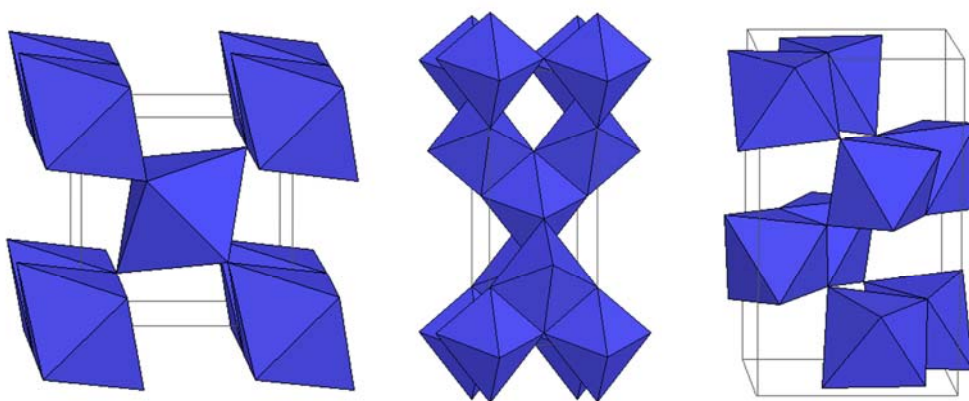


Figure 2 The crystal structure of rutile (left), anatase (middle) and brookite (right)

It is generally assumed that anatase allows a higher photocatalytic activity than rutile and brookite³. One of the reasons why the anatase type titanium dioxide is more photoactive than the rutile type may be the differences in their so called energy band structures. For anatase-type titanium dioxide this energy is 3.2 eV , which corresponds to UV light (388 nm), while the band gap energy for rutile type is 3.0 eV , corresponding to violet light (413 nm). The band gap energy for a semiconductor indicates the minimum energy of light to produce conduction band electrons and valence band holes. Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials.

The valence band energies for anatase and rutile are both similar, low in the energy diagram, meaning that, for both materials, the VB holes (and hydroxyl radicals $\cdot\text{OH}$) have great oxidizing power. The difference between anatase and rutile is in a conduction band. The conduction band for anatase is higher than for rutile in the energy diagram (Figure 3), meaning that it has higher reducing power. This means that it can drive very important reaction involving reduction of molecular oxygen O_2 to superoxide $\text{O}_2^{\cdot-}$. This issue is further discussed in the chapter 2.3.1.

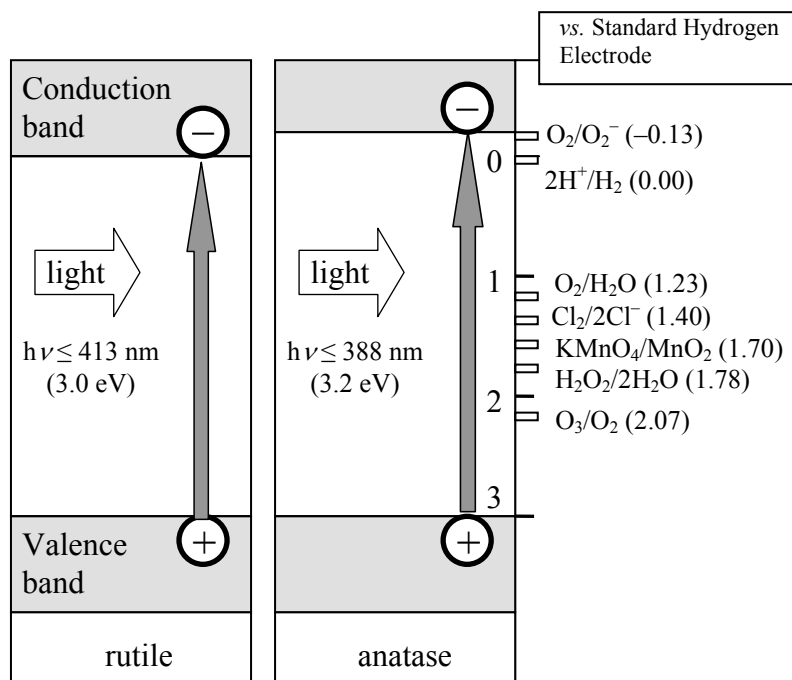


Figure 3 Energy diagram for TiO_2 and relevant redox potentials

2.3 Titanium dioxide photocatalysis

2.3.1 Oxidation-reduction reactions

The reaction starts with the exposure of titanium dioxide to light. As mentioned before (Chapter 2.1), two types of carriers are generated – electrons e^- and holes h^+ . On semiconductors such as TiO_2 these two survive for longer periods of time than e.g. in electrically conductive materials. On the surface of the catalyst, there is approximately a single layer of tightly adhering adsorbed water molecules. When these adsorbed water molecules are oxidized by holes, hydroxyl radicals $\cdot\text{OH}$ are formed (see Figure 5). The hydroxyl radicals can then react with organic compounds, producing free radicals, which are unstable molecules with one unpaired electron. When molecular oxygen with unpaired electrons is present, it likes to react with these free radicals, producing organic peroxy radicals. These can then take part in chain reactions, where organic compounds are completely degraded into carbon dioxide and water in a short time. The longer the film is illuminated with UV light, the more organic material can be decomposed (Figure 4, where E_{bg} is the band gap energy of the semiconductor)^{4,5}.

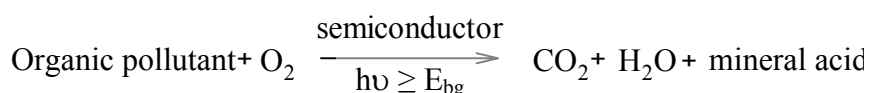


Figure 4 The basic process of semiconductor photocatalysis

The electrons that are produced in the electron-hole pairs are also put to work. These electrons are used to add electrons (reduce) to oxygen in the air. Oxygen is reduced easier than water to produce superoxide radical anion $\text{O}_2^{\cdot-}$. This $\text{O}_2^{\cdot-}$ attaches peroxy radicals resulting unstable product containing now at least four oxygens, that can decompose

to produce a carbon dioxide molecule. Superoxide acts like a “supercharger”, greatly increasing the oxidation process.

In general, organic compounds are more likely to be oxidized than water. Therefore, when the concentration of the organic compound is high, the photogenerated holes will react directly with these compounds (holes are effectively trapped) instead of reacting with water to produce $\cdot\text{OH}$, which increases the overall efficiency. Consequently, the rate-determining step is a speed of the transfer of electrons to oxygen.

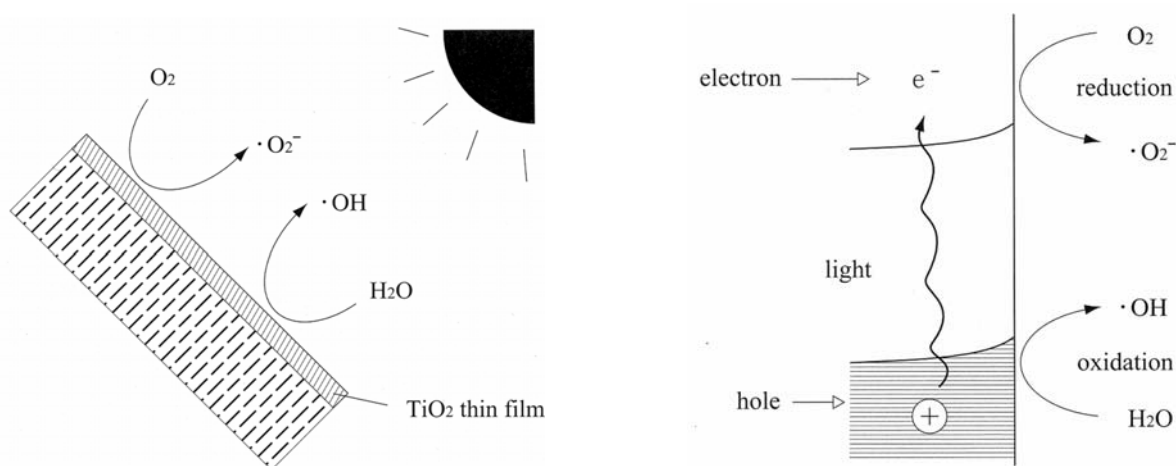


Figure 5 Reaction mechanism of TiO_2 photocatalysis

2.3.2 Characteristics of photocatalytic processes

Titanium dioxide is chemically activated by light energy. For a long time, photoactivity has been considered a problem, as titanium dioxide was used as a pigment. It decomposes organic materials that come in contact with it. This effect gives rise to the phenomenon of paint chalking, where the organic components of the paint break down as a result of photocatalytic action.

On the other hand, titanium dioxide photoactivity plays a positive role – decomposing materials of our choice, e.g. dirt, toxic chemicals, bacteria, etc⁴.

Titanium dioxide is widely used in the area of environmental photocatalysis and for its photoinduced hydrophilicity¹. The photocatalytic technology is applied to the decomposition of materials that are carried to the surface from surrounding environment. The superhydrophilic effect, on the other hand, is based on a concept of altering the properties of the surface itself by photocatalytic action. While both technologies are applied to the prevention of soiling, their basic mechanisms are quite different from each other (Figure 6). Hydrophilicity and photocatalysis take place simultaneously on the same TiO_2 surface but in varying proportions, depending on the desired application. It can be also concluded that the most appropriate applications for the photocatalytic approach would be those that involve low concentrations of matter that are of serious risks to health or comfort.

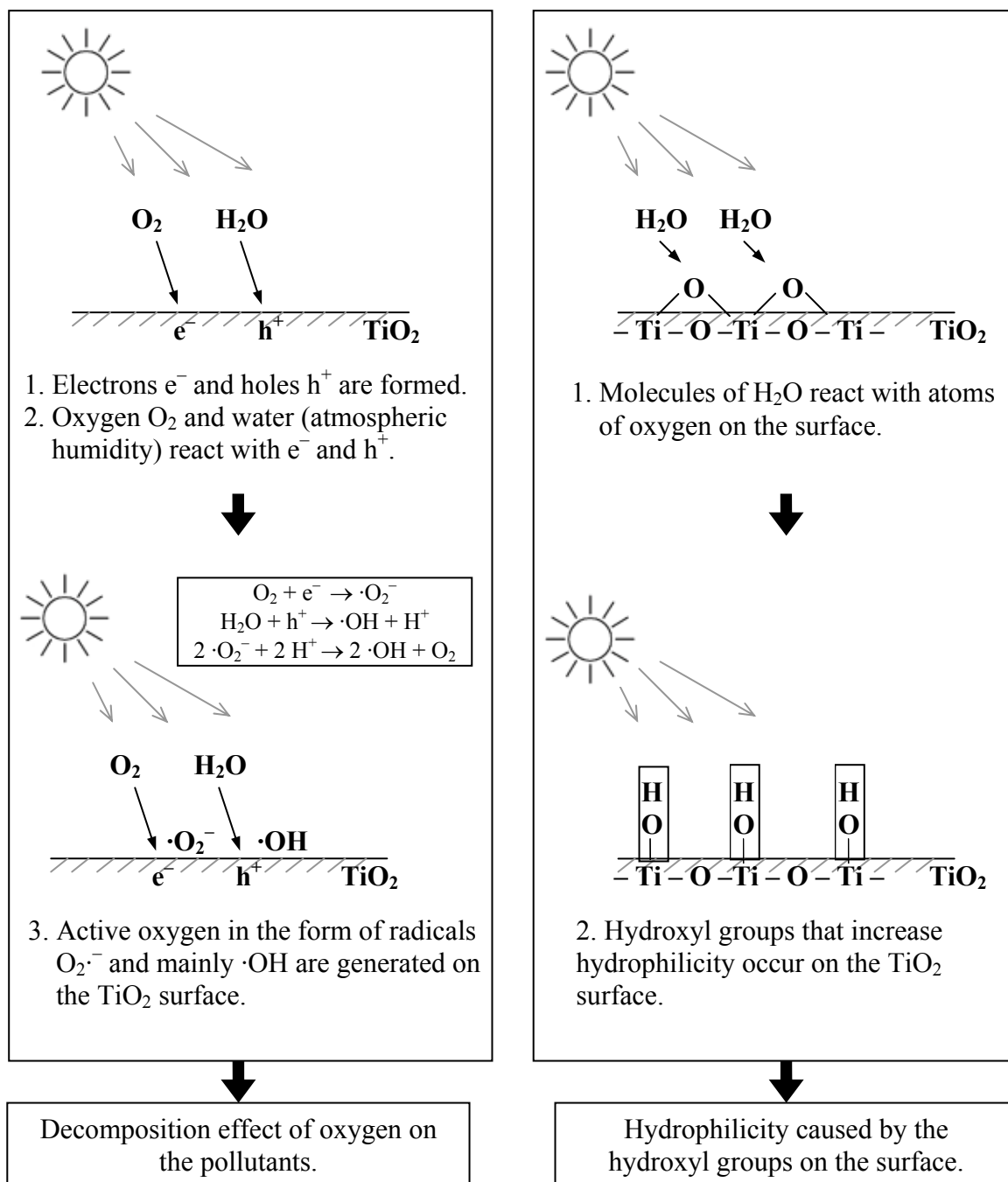


Figure 6 Characteristics of photocatalytic processes

2.3.3 Environmental semiconductor photocatalysis

The use of titanium dioxide in photocatalysis is dependent on the absorption characteristics, which allow it to absorb photons of UV light, producing reactive electron-hole pairs that can react with surrounding materials. The durability and stability of TiO_2 during such reactions make it an ideal material for any application where the material is to be used continuously without frequent replacement⁶.

Some of the applications and supporting technology have been reported in the literature, including the development of TiO₂ films, TiO₂-containing paper or tiles with photocatalytic antimicrobial and stain resistant surface were fabricated. Another application in photocatalytic technology is flow-type photoreactor for water purification. Also self-cleaning TiO₂-coated glass covers for highway tunnel lamps, self-cleaning window glass and building materials or TiO₂-containing self-cleaning paint should be mentioned.

Self-cleaning materials based on photocatalysts are able to clean without toxic chemicals, which is definitely a great advantage. However, these materials cannot do miracles; buildup of dirt can occur if the deposition of contaminants is faster than the speed of their decomposition. Also, if the dirt thickness is too high, no light can reach the titanium dioxide surface, than no reaction occurs⁴.

2.3.4 Photo-induced superhydrophilicity

The term superhydrophilicity actually means high wettability after UV illumination. On glass or other inorganic materials, water has a contact angle ranging from 20 to 30 degrees. With plastic, the contact angle is typically from 70 to 90 degrees.

A thin film composed of titanium dioxide photocatalyst combined with suitable additives shows an initial contact angle for water of several tens of degrees. When exposed to UV light, water starts to exhibit a decreasing contact angle; it tends to spread out flat. The best hydrophilic surface is that of zero contact angle, meaning that water spreads perfectly across the surface. At this stage, the surface becomes completely non-water-repellant and is said to be superhydrophilic.

The surface retains a contact angle of few degrees for water for a day or two without being exposed to ultraviolet light. Then the contact angle slowly increases and the surface becomes hydrophobic again. The superhydrophilicity can be recovered simply by exposing the surface to the UV light again⁴.

Also other liquids, as glycerol trioleate, hexadecane, ethylene glycol or tetralin, were used to measure contact angle. It was discovered that all mentioned liquids spread out, from which we conclude that UV illumination creates amphiphilic titania surface.

This phenomenon called superhydrophilicity is at present attributed to the production of “oxygen defects” on the surface of the titanium dioxide. Oxygen atoms are ejected and these photoinduced oxygen vacancies are replaced by dissociated water molecules, resulting in hydrophilic surface (Figure 7). One of the benefits of superhydrophilicity is the fact that, as the surface is less likely to form water droplets, it dries quickly. This effect occurs on indoor glass panels, where the formation of dew (usually in winter) can be prevented.

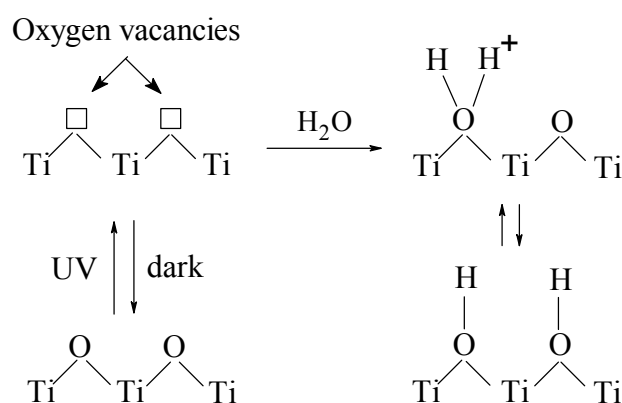


Figure 7 Mechanism of photoinduced hydrophilicity

2.4 Immobilization of TiO₂

TiO₂ can be used in a form of powder; however, it is not practical because of the post-treatment separation requirement, mainly because of formation of aggregates³. Thereby attempts have been made to immobilize TiO₂ particles in a form of a film, though the film-type photocatalyst exhibits lower activity than the powder form due to its relatively small specific surface area.

The films can be deposited on different solid supports as silica, soda lime glass, stainless steel paper, textiles and other materials. Several physical and chemical techniques as sputting, chemical vapor deposition, spray pyrolysis or sol-gel deposition can be used to obtain thin films. The widely used one is sol-gel method⁷.

2.4.1 Sol-gel method

Sol-gel method is one of the methods for preparing photoactive layers. It has many advantages over other methods mainly because of following: no special apparatuses are required; uniform multicomponent films can easily be formed if a homogeneous solution is available; the resultant films are characterized by a porous structure of a gel with a large specific area characteristic.

Sol is a dispersion of solid particles (~ 0.1–1 μm) in a liquid. Sol for TiO₂ film preparation contains a titanium source, alkoxide (e.g. tetraethylorthotitanate, tetrabutyltitanate, titanium tetraisopropoxide). Alkoxides are organometallic compounds of chemical formula M(OR)_n, where M stands for a metal and OR is an alkyl group. Alkoxide is then dissolved, usually by an alcohol, which brings water into the system. Water, which is needed for hydrolysis, does not break the solution homogeneity.

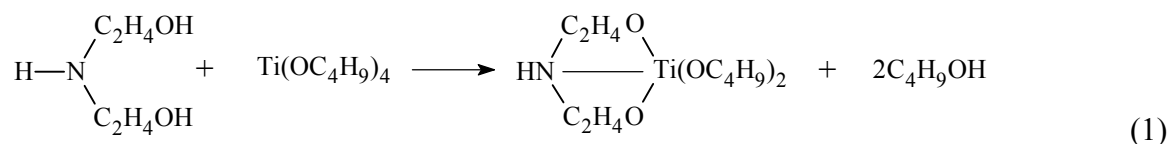
Sol is then deposited on a substrate (e.g. by spraying, dipping or spinning). The particles in sol are polymerized and produce gel in a state of a continuous network.

With further drying and heat treatment, the remaining organic and inorganic components are pyrolyzed and form an amorphous or crystalline coating^{8,9,10}.

The process of TiO₂ deposition, which also includes the sol-gel process, runs in few steps. The whole process will be described on the reactions of tetrabutylorthotitanate Ti(OBu)₄ as a precursor and polyethylene glycol (PEG) as a template.

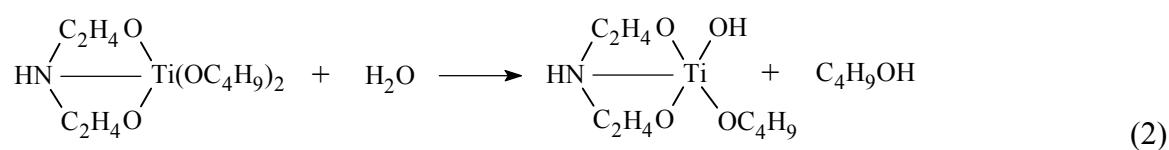
First the complexing reaction of the Ti(OBu)₄ precursor and the complexing agent diethanolamine takes place.

1. Complexing reaction

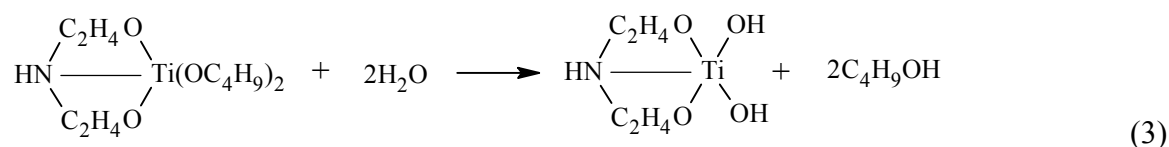


In another step water is added resulting in hydrolysis and polycondensation reaction of Ti(OBu)₄ precursor:

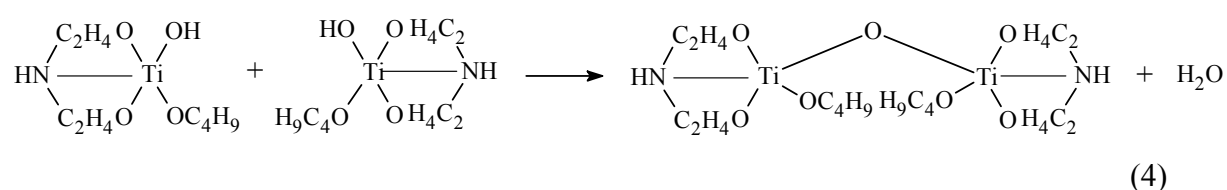
2. Hydrolysis



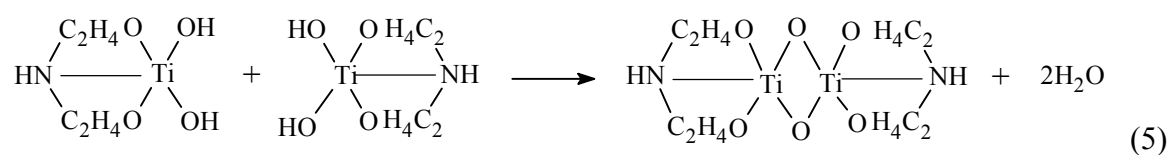
or



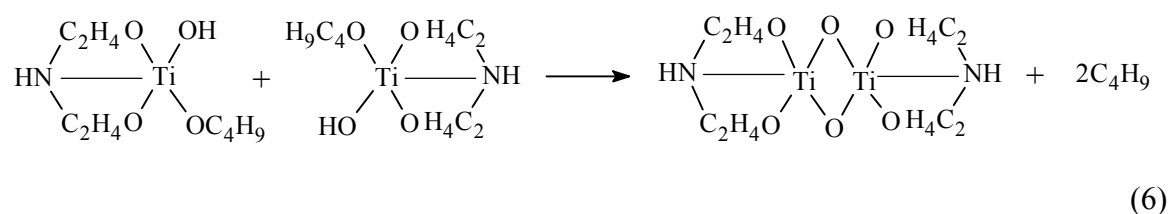
3. Dehydration polycondensation



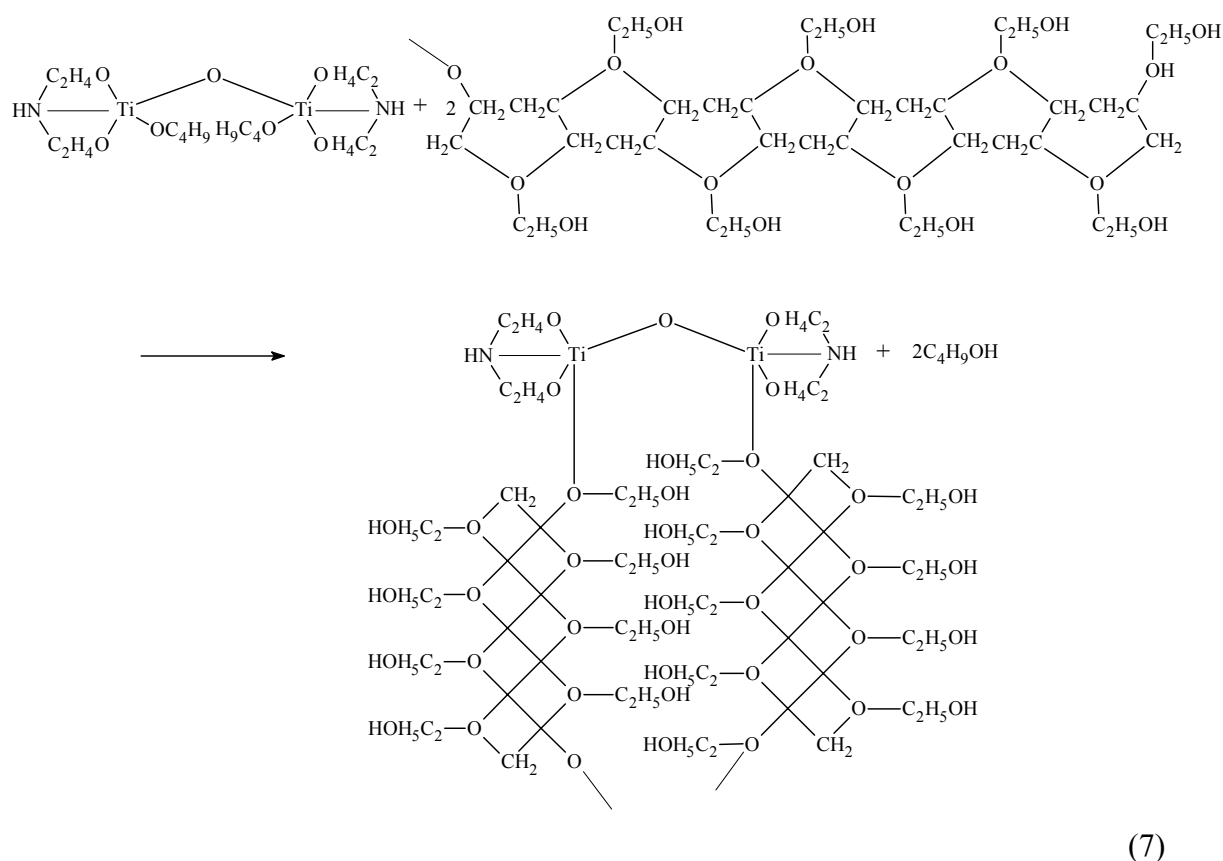
or



4. Debutanation polycondensation



Then polyethylene glycol is added into the TiO_2 sol, which plays a role of the structure-directing agent. PEG helps to form an inorganic-organic network, leading to the original morphology of TiO_2 porous films:



Finally the TiO_2 sol is deposited on a substrate and undergoes calcination, resulting in the removal of all the organic substances¹¹.

2.5 Aspects effecting the TiO_2 film structure

In majority of TiO_2 -coating applications accessibility to a crystalline surface is of prime importance. Therefore the production of an open, highly porous titanium dioxide network in either the anatase crystalline phase is desirable because (1) the high surface area allows maximum contact between the TiO_2 network and the reaction medium and (2) the continuity of the network prevents traps from depleting its efficiency. The preparation of thin films with good control of pore size distribution, and without delamination or cracking in the calcination process is technically challenging but there have been a few successful examples. The success in obtaining a specific mesoporous metal oxide depends on two factors: (1) the occurrence of a three-dimensional mesophase and (2) the stability of the metal oxide framework upon the removal of the surfactant species^{13,12}.

2.5.1 Effect of structure-directing agents

In order to obtain well-defined mesoporous structure and better control on porous size and porosity of the resultant material, various structural directing reagents (SDR) have been introduced to sol-gel processes. These SDR are capable of forming long-range 3D nanosize networks, which can be used as structural templates to define a mesoporous structure. The synthesis of large-pores M- TiO_2 remains as a challenge due to the rapid hydrolysis of titanium precursor that is difficult to control. In practice, strong acids are commonly employed to reduce the rapidity of the hydrolysis process. Recently, weak acids replaced strong acids for better control of the hydrolysis process of titanium source¹³. Also chemical modification

of transition metal alkoxide precursor by acetylacetone leads to slowing down the above mentioned sol-gel process and thus stabilizes the sol¹⁴.

Porous inorganic TiO₂-anatase films can be obtained using conventional alkoxide sol-gel route with the addition of surfactants¹⁵. The interaction between the surfactant and the inorganic wall should not be too strong, so that the mesostructure assembly can take place and the surfactant can be removed easily without damage to the integrity of the channel walls. For this purpose, hydrogen bonding, and/or weak coordination bonds are more preferred than electrostatic interactions and covalent bonding¹⁴.

The templates permit to retain the initial polymer morphology up to final porous structure. Polyethylene glycol is especially suitable for modifying the porous structure of coatings due to its complete decomposition at relatively low temperature. However, the control of synthesis and deposition processes is crucial for obtaining thick, crack-free and homogeneous coatings. Crystalline phase, specific surface area, surface OH groups, morphology and aggregation of particles are some of the parameters playing a decisive role in the photocatalytic efficiency of titania. However, diverse results can be found in literature. While some authors highlight the high surface area as determining factor to increase efficiency, others point out the influence of crystallinity and particle size.

Taichens et al. found that the mean crystalline size decreased from 17 to 13.3 nm when the molar weight of PEG increased from 200 to 20 000. They also investigated the effect of PEG molecular weight on the pore size distribution. It was found, that an increase in the PEG molecular weight leads to a stepwise increase in the pore size range¹³.

Arconada et al. prepared two films, one without PEG and the other one with added PEG. Both prepared sols were homogeneous and transparent. It was observed that the incorporation of PEG permits to reduce the sintering time needed to clearly observe the anatase crystal phase. They also found out that inclusion of PEG increases porosity, which causes an augment in photoactivity of the film. The addition of PEG and its further elimination during the heat treatment lead to an increase of surface area and porosity of the sample reducing the internal mass transfer limitation of the pollutant to the active sites¹⁴.

Arpi et al. prepared TiO₂ thin films on glass substrate by sol-gel technique with a very small variation in the PEG concentrations in order to study the gradual change in the structural, optical and surface morphological properties. The crystallite sizes increased from 12.3 nm to 13.3 nm for the TiO₂ film, deposited without PEG and with 0.3 g of PEG. The film without PEG has more compact structure with high density of crystallite. While for TiO₂ film with the same number of coatings, introduction of PEG induces porous structure with less number of crystallites. Interestingly, the presence of PEG does not inhibit the crystallization but on the contrary it helps the growth process. The formation of porous network structure is due to the fact that the sol particles formed by the sol-gel reaction were covered by PEG chains to form an inorganic/polymer composite through physical cross-linking and agglomeration of particle-PEG complexes. While calcined under high temperature, PEG was demolished from the composites and left a porous network with higher roughness of the surface. The photocatalytic activity improves¹⁶ with the increased crystal size, induced porosity and rough open surface due to the increased amount of PEG.

Guo et al. also used PEG for the TiO₂ film preparation. The films were crack-free and strongly adherent to the substrate after calcinations, contrasting strongly with the flaky and crack laden films formed without the PEG. It is believed that PEG is completely destroyed at 550 °C. The thermal decomposition of the polymer resulted in the creation of pores among the TiO₂ aggregates. The pores were elongated and irregularly shaped, with sizes falling

in the range of about 100 nm. As water was added together with PEG in the hydrolysis mixture, some water molecules would associate with PEG through hydrogen bonding, loosening the PEG chains in due course. The free, non-associated water molecules were readily available to the titanium tetraisopropoxide (titanium source) for hydrolysis in the early stages¹¹.

Narayanaswamy et al. used tetraethylortotitanate as a titanium source and cetyltrimethylammonium bromide as a cationic surfactant. They prepared titania-based materials with a worm-like framework and high surface area with presence of close-packed nearly hexagonal macropores, which are formed by the agglomeration of TiO₂ nanocrystals. The macropores allow easy access of materials to the entire mesopore network, since every part of the network is near a macropore, which could conceivably facilitate a catalytic process by allowing faster flow of materials through the TiO₂ network⁶.

2.5.2 Effect of calcination temperature and calcination time

Two different methods of heat treatment are usually used if more layers are deposited: (1) annealing of each layer at a temperature sufficient for crystallization of the film or (2) drying of the titanium oxide film mostly at 100–150 K after each layer deposition in order to remove the solvent and subjecting to high-temperature heat treatment only after the deposition of the last layer. Kuynetsova et al. studied these two approaches and said that a large number of cavities in the sample can be due to the prolonged drying resulted in the solvent evaporation before the high-temperature treatment. Evaporation of the solvent from the gel film affects the morphology. A sol film is required to have a sufficient fluidity for some time during the drying process to form macroporous structure. As prepared film is porous not only on the surface but also in the bulk, so the film is thick enough to make possible the formation of a three-dimensionally interconnected sponge-like pore structure¹⁴.

Taichen et al. found that an increase in the treatment temperature results in an increase in the crystallinity. The mean crystalline size increased from 9.8 to 36 nm when the treatment temperature was increased from 350 to 650 °C. The pore size is the smallest at 350 °C-calcined sample. The pore size is higher with increasing calcination temperature, which is due to the mesoporous structure consolidation as a result of improved crystallinity. It was also observed that for the sample calcined at 650 °C aggregates of plate-like structure exist and that the mesoporous structure is completely collapsed, nonporous¹³.

Arconada et al. studied the evolution of crystalline fraction as a function of temperature and time of the heat treatment. An important increment is observed for short treatments, associated with the rapid formation and/or growing of anatase crystals. Above 3 hours of heat treatment, the crystalline fraction maintains quite constant for $T \geq 400$ °C. Coatings treated at 350 °C need a longer time (10 hours) for total crystallization.

They also explained the relation between the coatings thickness and the calcination temperature and time. The coating thickness decreased with temperature and time of the thermal treatment due to the concentration of the network associated with the sintering process.

Other relevant property related with photocatalytic activity is the specific surface area S_s . At 350 °C low S_s are observed probably due to the incomplete removal of organic residues, still present in the structure. Above this temperature, S_s increases up to the maximum situated around 400–450 °C. Higher treatment temperatures reduce the photoactivity of the coatings.

These results indicate that the photoactivity of titania coatings is closely related with S_s . Although the presence of anatase is necessary, the crystal fraction and crystal size seem not to

play a critical role in photocatalyst behavior. These conditions implicate a compromise in temperature and time of sintering to ensure the appearance of TiO₂-anatase crystal phase, maintaining the high porosity of the layer¹⁵.

Sudgahar et al. has reported that the metal precursor concentration of the sol and the calcination temperature highly influences the film surface and other physical properties. They prepared two films A and B. The film A corresponds to a lower metal precursor concentration. The film A has a lower thickness and for both A and B the increased calcination temperature leads to a decrease in a thickness¹⁴.

Guo et al. also proposed results of thermal analysis of TiO₂-PEG composites as weight losses against temperature. The first weight loss at temperatures below 100 °C was clearly the removal of physisorbed water. The second weight loss between 200 and 300 °C could be attributed to the expulsion of organics. The removal of structural water came in last between 300 and 400 °C, with subsequent increase in the number of bridging oxygen and thus the monolithic nature of the gel matrix. The presence of PEG in the xerogel had apparently raised the temperatures of corresponding weight loss events in the PEG-free xerogel. As result, the gel became more thermally stable with the increase in the PEG content¹¹.

2.6 Piezoelectric deposition

Inkjet printing is a non impact dot matrix printing technology in which droplets of ink are jetted from a small aperture directly to a specified position on a media to create an image. Inkjet printing is a very simple technique for preparing a coated substrate, it is widely used in printed electronics because less manufacturing steps are needed, less material waste is produced and also because of cost savings¹⁷.

There are two methods for inkjet printing with many variations within each. The first one is a Continual Stream (CS) technique (Figure 8) whereby a continuous ink stream is broken into droplets of uniform size and spacing. An electric charge is impressed upon the drops selectively. The charged drops when passing through an electric field are deflected into a gutter and recirculated while the uncharged drops fly directly to the media to form an image.

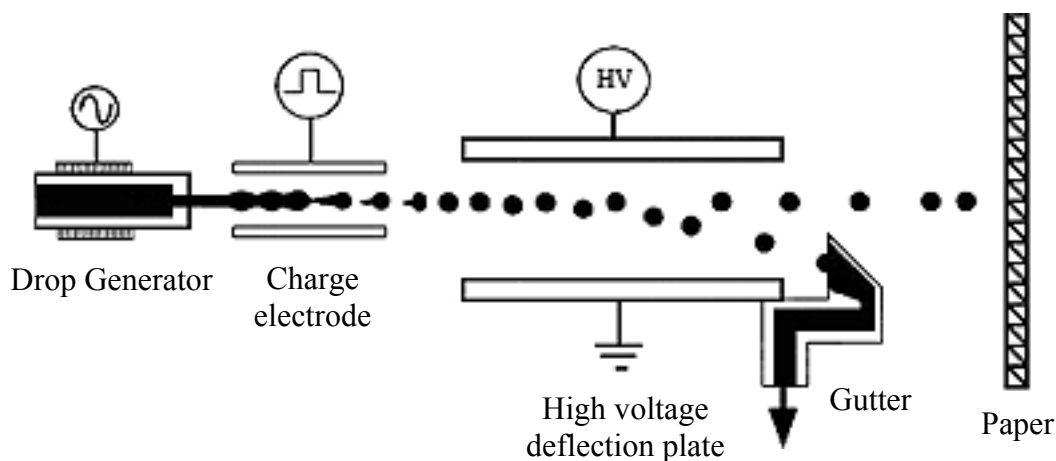


Figure 8 Continual Stream (CS) inkjet printing technique

The second inkjet printing method is a Drop-on-Demand (DOD) technique. DOD technology allows the print head to generate ink droplets only when the drop is needed to create an image on a media. There are four methods of DOD inkjet printing: thermal,

piezoelectric, electrostatic and acoustic. Most of the inkjet printers on the markets today use either the thermal (Figure 9) or piezoelectric principal (Figure 10).

Thermal inkjet printing, commonly referred to as bubble jet, is a method where ink drops are ejected from a nozzle by the growth and collapse of a water vapor bubble on the top surface of small heater located near the nozzle^{18,19}. When an ejected ink drop collapses, a vacuum is created. This pulls more ink into the print head from the cartridge. Thermal technology is best suited for applications where low ink volumes are required such as home and office.

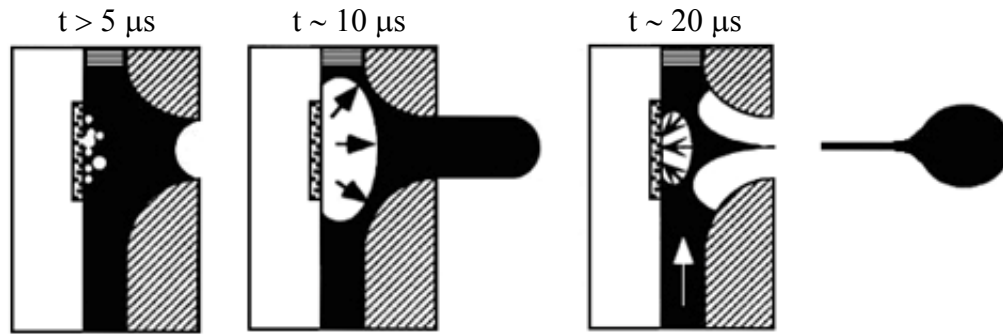


Figure 9 Thermal Drop-on-Demand inkjet printing method

Piezoelectric drop-on-demand printing is patented by Epson. This method uses the deformation of piezoelectric material to cause an ink volume change in the pressure chamber. The piezoceramics receives a tiny electric charge that causes it to vibrate²⁰, which initiates a sudden volume change. The volume change generates a pressure wave that propagates toward the nozzle. This acoustic pressure wave overcomes the viscous pressure loss in the small nozzle and the surface tension force from the ink meniscus so that an ink drop can be ejected from the nozzle.

If this technique is used as a thin layer deposition method, some necessary printer features should be met:

- Piezoelectric print heads
- Printheads separated from ink tanks
- Individual ink tanks
- Capability of printing onto rigid substrates (CD/DVD)
- Software – one channel printing

There are also some requirements on the „ink“ properties²¹:

- No aggressive components (corrosive acids or bases, corrosive org. solvents)
- Solid particles must be significantly smaller than ink nozzle orifices (usually 20–30 μm)
- Solid particles aggregation must be prevented

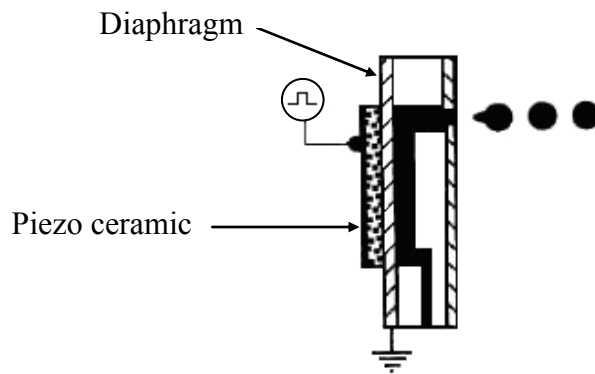


Figure 10 Piezoelectric Drop-on-Demand inkjet printing method

2.7 Pre-treatment of soda-lime glass support

When a transparent thin film of titanium dioxide is formed on a surface, an organic compound containing titanium is thermally decomposed. The temperature is raised to about 400 °C so that a hard film of titanium dioxide can form on the glass support. However, if the temperature is raised too far, the soda-lime glass begins to soften and the sodium ions slowly diffuse from the glass and form a sodium-titanium-oxygen compounds, which does not have photocatalytic activity (Figure 11).

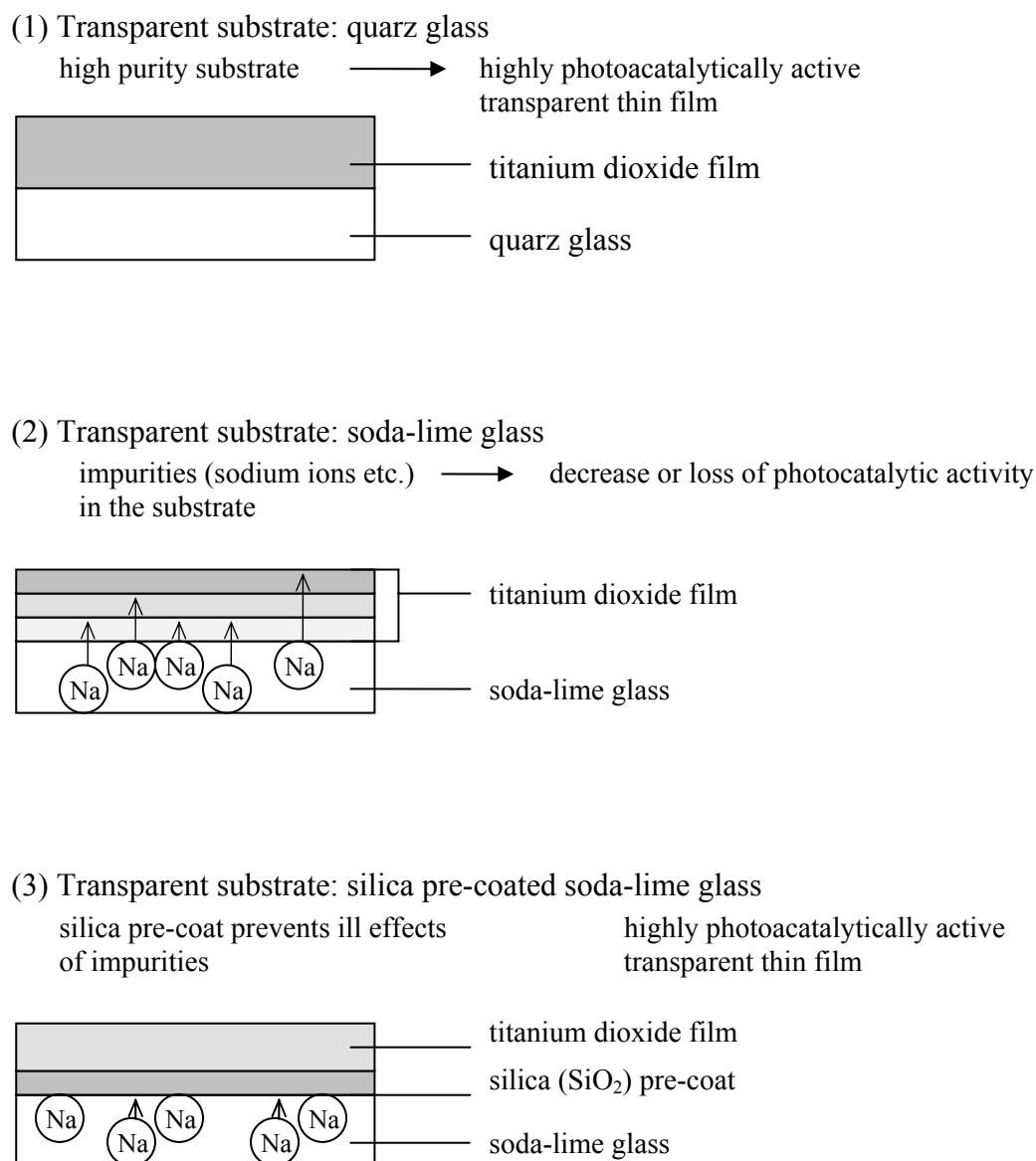


Figure 11 Preparation process for transparent self-cleaning glass

Sodium diffusion needs to be blocked. One of the successful methods is application of silicon dioxide (pure silica glass) layer as a pre-coat¹⁵. Another possibility is to acid the glass substrate, in other words, to boil the glass substrate in acid, mostly in hydrochloric acid (HCl) or sulfuric acid (H_2SO_4)^{22,13}.

2.8 Kinetics of heterogeneous photocatalytic reactions

Heterogeneous photocatalytic process is a reaction between a photoinduced charge carriers and an adsorbed reagent on the photocatalyst surface (solid phase), which evokes chemical changes of the reactant (gaseous or liquid phase). The photocatalytic reaction runs in partial sequential steps²³:

- reagent transport from the liquid (gaseous) phase to the photocatalyst surface
- reagent adsorption on the photocatalyst surface

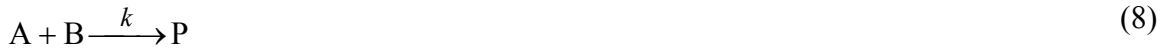
- chemical reaction on the photocatalyst surface
- product desorption from the photocatalyst surface
- product transport into the liquid (gaseous) phase.

The overall reaction rate depends on the reaction rate of each individual step of the whole process. Reagent transport to the photocatalyst surface is caused by convection and diffusion, in other words, it generally depends on the hydrodynamic and diffusive character of the system (gas or liquid circulation, particle size, diffusion coefficients, etc.). Diffusion of the reagent through the porous structure of the solid photocatalyst depends on the pore size, particle size, diffusion coefficients and concentration gradients of the reagents.

The transport rate of the reagents is higher than the reaction rate in the reactor; therefore it is not the determining step for the overall reaction rate. The overall reaction rate is mostly dependent on the reagent adsorption and the chemical reaction on the solid photocatalytic surface.

2.8.1 Langmuir-Hinshelwood

Langmuir-Hinshelwood (LH) kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes²⁴. In LH models, the surface of the catalyst is modeled as being energetically uniform, and it is assumed that there is no energetic interaction between species adsorbed on the surface. Each reactant is assumed to adsorb on a surface site. Following surface reaction between adsorbed reactants to generate surface products, the products desorb from the surface²⁵. Heterogeneous surface catalytic reaction mechanism is based on the reaction between molecular fragments and atoms adsorbed on the catalyst surface. Therefore, these reactions are the second order reactions¹⁰:



The reaction rate is:

$$v = k \cdot \theta_A \cdot \theta_B \quad (9)$$

Using the Langmuir isotherms for A and B, the adsorption runs without dissociation:

$$\theta_A = \frac{K_A \cdot c_A}{1 + K_A \cdot c_A + K_B \cdot c_B} \quad (10)$$

$$\theta_B = \frac{K_B \cdot c_B}{1 + K_A \cdot c_A + K_B \cdot c_B} \quad (11)$$

where θ is a concentration of sites covered with A or B. K_A , K_B are the adsorption constants of the reactants A and B; c_A and c_B are concentrations of A and B.

Applying the expressions (10) a (11) on the expression (9), we obtain for the reaction rate v following equation:

$$v = \frac{k \cdot K_A \cdot K_B \cdot c_A \cdot c_B}{(1 + K_A \cdot c_A + K_B \cdot c_B)^2} \quad (12)$$

The rate constant k and isothermal parameters K_A and K_B are thermally dependent.

The kinetics of the heterogeneous catalytic reactions can be simply qualified by the reaction rate equation (Langmuir-Hinshelwood equation):

$$v = \frac{k \cdot K \cdot c}{1 + K \cdot c} \text{ (per gram of photocatalyst)} \quad (13)$$

For practical application a linearized equation (13) is used. This is obtained using the dependence of reciprocal initiative rate over reciprocal initiative concentration:

$$\frac{1}{v} = \frac{1}{k} + \frac{1}{k \cdot K} \cdot \frac{1}{c} \quad (14)$$

At lower concentrations, reaction is simplified to the first order:

$$v = k \cdot K \cdot c \quad (15)$$

The reaction rate is now dependent only on the concentration, because k and K are constants of the process.

When applying the equation (12) for the dosing reactor, following dependence is obtained:

$$-V \cdot \frac{dc}{dt} = \frac{m \cdot A \cdot k \cdot K \cdot c}{1 + K \cdot c} \Rightarrow -\frac{m \cdot A}{V} \cdot t = \frac{1}{k \cdot K} \cdot \ln \frac{c}{c_0} + \frac{c - c_0}{k} \quad (16)$$

where V is a volume of fluid, A is a number of adsorption sites per gram of the catalyst and m is a mass of catalyst. From this equation, it is possible to calculate the time needed for reduction of concentration c_0 to $c_0/2$, which is defined as half-time $\tau_{1/2}$:

$$\tau_{1/2} = \frac{\frac{\ln 2}{k \cdot K} + \frac{c_0}{2 \cdot k}}{\frac{m \cdot A}{V}} \quad (17)$$

If the concentration $c_0 \ll 1/K$, the reaction is always of the first order and the half-time does not depend on the initiative reagent concentration c_0 but only on the catalyst concentration (m/V) and its reactivity (k, K).

In some cases, when the reactant is insoluble in water ($c \approx 0$), the reaction is specified by the following equation:

$$v = \frac{d(c_{\text{ads}})}{dt} = -k \cdot (c_{\text{ads}}) \quad (18)$$

The half life of the reaction is than:

$$\tau_{1/2} = \frac{\ln 2}{k} \quad (19)$$

where k is a slope of a linear function $\ln(c_{A0}/c_A) = f(t)$, which runs through zero. Another important parameter for comparing rates of particular reactions is a conversion rate α :

$$\alpha = \frac{c_0 - c_t}{c_0} \quad (20)$$

2.9 Chemical reactors

The type of used reactor depends on the physical properties and chemical reactivity of the substances that come into the reaction. If a reactor for photocatalytic reaction is used, the selection of the reactor material is very important. Photons are present at the photocatalytic reaction, so the radiation has to pass through the reactor material without any loss of intensity. The irradiation spectrum should be equal to the absorption spectrum of the photocatalyst. If a semiconductor photocatalyst is used, the energy of the absorbed radiation should be equal or higher than the energy of the semiconductor bandgap.

The reactors can be divided according to the movement of the reaction mixture inside the reactor. Continuous (flow) reactors use continuous feeding of a substance and also continuous withdrawing of a product which makes the mass inside the reactor circulate. On the other hand, if a reactant is dosed at the beginning of the reaction and a product is withdrawn at the end of the reaction, we talk about discontinual (batch) reactors^{23,26}.

2.10 Instruments for TiO₂ films characterization

2.10.1 UV/VIS spectrophotometry

UV/VIS spectrophotometry is used to determine the absorption or transmission of UV/VIS light by a sample. It can also be used to measure concentrations of absorbing materials based on developed calibration curves of the material.

The UV/VIS spectrophotometer is employed to measure the amount of light that sample absorbs. It uses two light sources, a deuterium (D₂) lamp for ultraviolet light and a tungsten (W) lamp for visible light. The light beam passes through a group of slits and mirrors, after that it splits into two beams. One of the beams is allowed to pass through a reference cuvette with solvent, the other passes through the sample cuvette. The intensities of the light beams are then measured at a detector.

The change in intensity of light dI after passing through a sample should be proportional to the path length db [cm], concentration c [mol·dm⁻³] of a sample and intensity of the incident light I . Thus, dI is proportional to $b \cdot c \cdot I$:

$$\frac{dI}{I} = -k \cdot c \cdot db \quad (21)$$

$$-\int_{I_0}^I \frac{dI}{I} = k \cdot c \cdot \int_0^b db \quad (22)$$

where k is a proportionality constant, I_0 is the initial intensity of the beam before entering a sample. Integration of this equation leads to Lambert-Beer law:

$$-\ln \frac{I}{I_0} = k \cdot b \cdot c \quad (23)$$

$$A = -\log \frac{I}{I_0} = \varepsilon_\lambda \cdot b \cdot c \quad (24)$$

where $\varepsilon_\lambda = 2,303 \cdot k$ is a molar absorption coefficient [dm⁻³·mol⁻¹·cm⁻¹]. A is defined as absorbance and is directly proportional to the path length b and the concentration

of the sample c . The molar absorption coefficient is characteristic of the substance under study and is a function of the wavelength. Molecules strongly absorb only in some regions of electromagnetic spectrum. The photon carries a specific amount of energy defined by its wavelength. The least energy of photon (the longest wavelength) corresponds to the energy difference between the ground and the first excited state (or promotion of an electron from the highest filled orbital to the lowest unfilled orbital).

2.10.2 Contact angle measurements

Measurement of contact angle provides a better understanding of the interactions between phases, regardless of whether they are gas, liquid or solid. The wettability and surface energy of solid surfaces plays an important role in many processes, such as controlled capillary action, spreading of coatings, adhesion and absorption into porous solids etc. Contact angle is a rapid and accurate characterization tool.

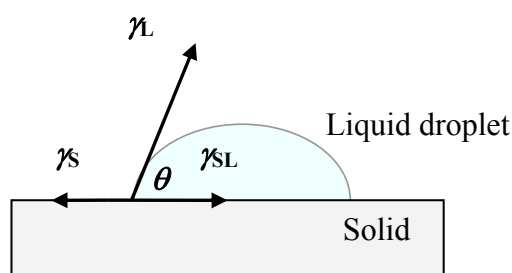


Figure 12 Interface/surface tensions between liquid and solid

Contact angle is a quantitative measure of the wetting of a solid by a liquid. It is a direct measure of interactions taking place between the participating phases. Contact angle is geometrically defined as the angle on the liquid side of the tangential line drawn through the three phase boundary where a liquid, gas and solid intersect. The shape of the drop and the magnitude of the contact angle are controlled by three interaction forces of interfacial tension of each participating phase (gas, liquid and solid) (Figure 12). The relation between these forces and the contact angle can be evaluated by the Young's equation²⁷:

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (25)$$

where θ is a contact angle, γ_S , γ_L , γ_{SL} are solid surface, liquid surface and solid/liquid interfacial free energy, respectively.

3 EXPERIMENTAL

3.1 Chemicals, devices and software

3.1.1 Chemicals

- Sodium 2,6-dichlorindophenolate hydrate (DCIP), A.C.S. reagent, Aldrich
- Titanium(IV)isopropoxide (TTIP), purum, Fluka
- Ethanol absolute p.a., Penta, Chrudim
- Acetylacetone p.a. (AcAc), Lachema, Neratovice
- Polyethylene glycol (PEG) 1500, Merck
- Sulfuric acid p.a., min. 93%, Lachema, Neratovice
- Deionized water

3.1.2 Devices

- Analytical scales Scaltec, SPB 32
- Contact Angle System OCA 10, DataPhysics
- Magnetic stirring device, Lavat Chotutice
- UV-VIS Spectrophotometer Spectronic Unicam, Helios α
- Radiometer X 97 with Radiometric Detector Head, Gigahertz-Optic
- Inkjet printer Epson R220
- Metal-halide lamp HPA 400/30 SD, R7S, Philips
- Black lamp Sylvania Lynx-s 11W BLB
- Pumping device PCD 83
- Electric hot plate

3.1.3 Software

- Microsoft Excel 2003
- Microsoft Word 2003
- Vision Scan, version 3.5

3.2 Titanium dioxide film deposition

3.2.1 Substrate pretreatment

Soda-lime glass (50×50×1.1 mm) was used as a substrate for the TiO₂ film deposition. The glass plates were boiled in sulfuric acid (50%) for 120 minutes to block the diffusion of sodium ions from the glass. The glass plates were rinsed with deionised water and dried.

3.2.2 Sol synthesis

The sol in the experimental procedure was prepared by the sol-gel method using AcAc as a stabilizing (complexing) agent, ethanol (absolute) as a solvent and PEG as a structure-directing agent.

The sol-gel solution was prepared as follows: TTIP (10.5 cm^3) was added dropwise to a solution of 40 cm^3 ethanol and 3.8 cm^3 AcAc at room temperature under vigorous stirring. After that a mixed solution of deionized water (0.69 cm^3) and ethanol (45 cm^3) was added dropwise to the above solution under stirring. Finally, exact amount of PEG (16 g.dm^{-3}) of the molar weight 1500 g.cm^{-3} was added to obtain sol for deposition. As prepared sol was stored at 5°C in a glass bottle wrapped in aluminum foil.

3.2.3 TiO_2 film preparation

The prepared titania sol was deposited on the soda-lime glass plates by piezoelectric deposition. Inkjet printer works under frequency-modulated screening, which means that the individual dots have the same diameter but are different distances apart (non-periodic screening). Tone values for printing are reproduced merely by varying the dot spacing and the ink film thickness on the substrate is identical for all dots²⁸. The inkjet printer enables deposition of various amounts of ink to obtain various values of relative dot area. Variations in the relative dot area values lead to the variation in grey levels of printed image, 100 % means that the whole surface is covered by ink and 0 % stands for an uncovered surface²⁹.



Figure 13 Inkjet printer Epson R220 and a CD holder

The TiO_2 layers were printed by the Epson inkjet printer (Figure 13). The above prepared sol was dosed into a refillable ink cartridge for black ink, the other cartridges were empty. Printer driver must enable „black only printing“. The glass substrate was fitted into an adopted CD holder and placed into the printer feeder. A square area ($40 \times 40 \text{ mm}$) was printed on the glass substrate in a "Rapid" printing mode. The rapid mode represents the 100% surface coverage and the picture definition of 360 dpi. The print head runs above the printed surface, which is deposited in both directions of the print head movement. The solvent vapors out of the layer even during the printing process (Figure 14).

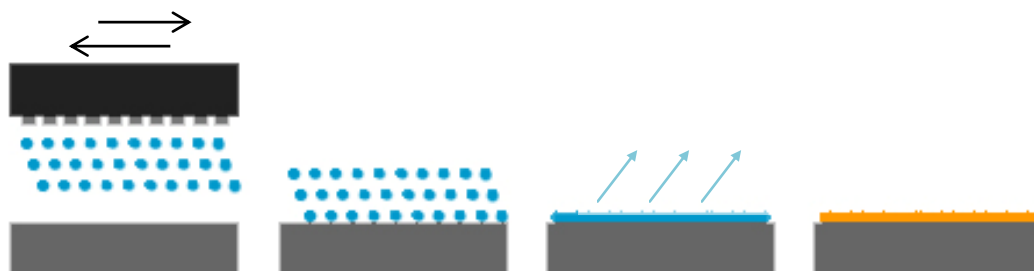


Figure 14 Rapid printing mode

The coated glass plates underwent gelation at 110 °C for 30 minutes. Finally calcination at 450 °C for 4 hours with a heating rate of 3 °C.min⁻¹ to obtain titania films (Figure 15).

Table 1 Basic data of the rapid printing mode

Deposition mode	Resolution (dpi)	Relative dot area (%)	Direction	Amount of PEG 1500 (g.dm ⁻³)
Rapid	360	100	bidirectional	16

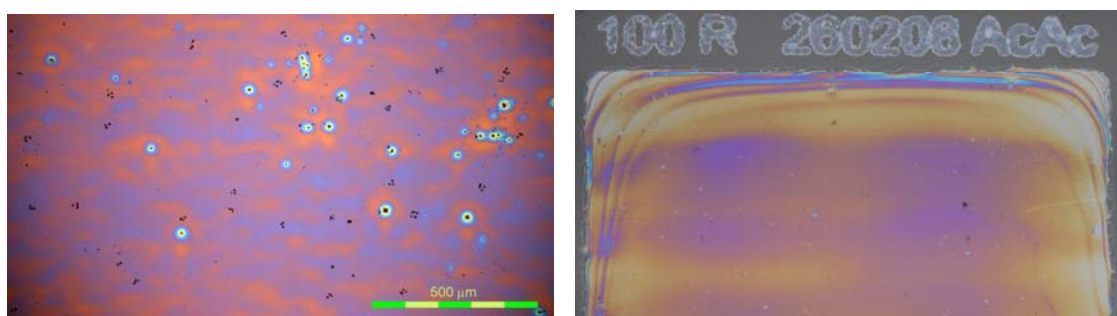


Figure 15 TiO₂ film with PEG 1500 (16 g.dm⁻³): Image in polarized light in the middle part of the film (left) and macro image of the film (right)

3.2.4 Photocatalytic activity of the TiO₂ films

The photocatalytic activity of the TiO₂ films were investigated by using 2,6-dichloroindophenol (DCIP). The volume of tested DCIP was 150 cm³, the initial concentration of DCIP was 2.10⁻⁵ mol.dm⁻³.

Two soda-lime glass plates A and B (50×50×1,1 mm), obtained by piezoelectric deposition, were placed into a plate reactor (Figure 16) and irradiated by one of the two lamps (sources of UV-light) for 15 minutes. Then the whole volume of DCIP solution was poured into the reactor. The glass plate has to be placed as close under the solution level as possible. The used plate reactor works with a continuous flow of the probed DCIP provided by a peristaltic pump. The obtained rate of flow was 1.3 cm³.s⁻¹ (4.8 dm³.hod⁻¹). Equal amounts of DCIP solution (3 cm³) were analyzed in 10-minute intervals.

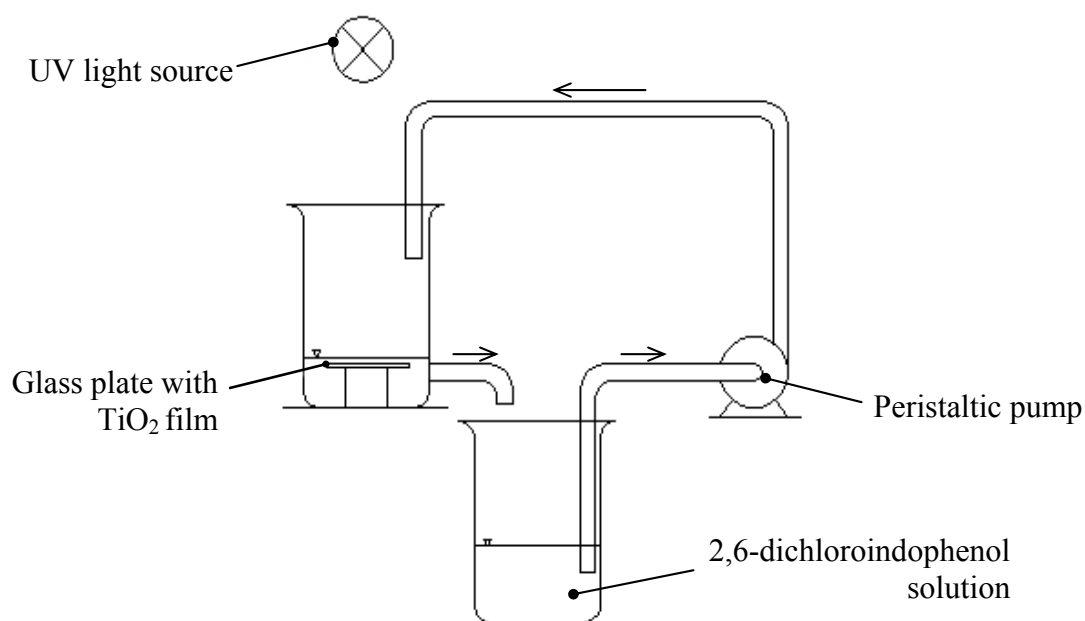


Figure 16 Scheme of the plate reactor

The decrease in DCIP concentration was measured by UV-VIS spectrophotometry (Figure 17). Absorbance was measured in the range of 190–700 nm. The maximum absorbance values obtained for different times of the DCIP degradation were used to calculate the formal first rate reaction constant.



Figure 17 UV-VIS spectrophotometer Helios α

Two types of lamps for the TiO_2 films irradiation were used as a source of UV light. Metal-halide lamp HPA 400/30 SD, R7S, Philips (Solar lamp) was placed above the reactor to set the constant intensity of the incident light on the glass substrate on the value of $4.5 \text{ mW} \cdot \text{cm}^{-2}$. The other lamp Sylvania Lynx-s 11W BLB (Black lamp) was fixed in a position to obtain the intensity of $3 \text{ mW} \cdot \text{cm}^{-2}$. The values of intensities were measured on the top of the glass substrate placed in the reactor. Emission spectra of the used lamps are shown in Figure 18 and Figure 19.

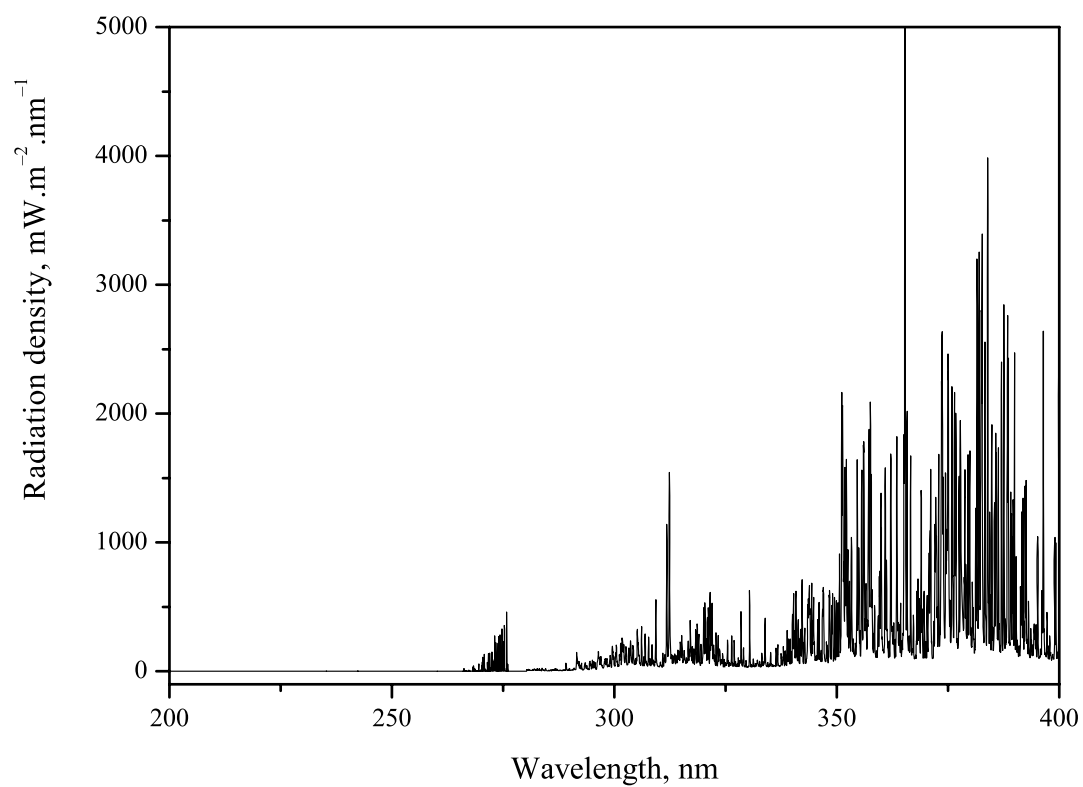


Figure 18 Emission spectrum of the metal-halide lamp HPA 400/30 SD, R7S, Philips

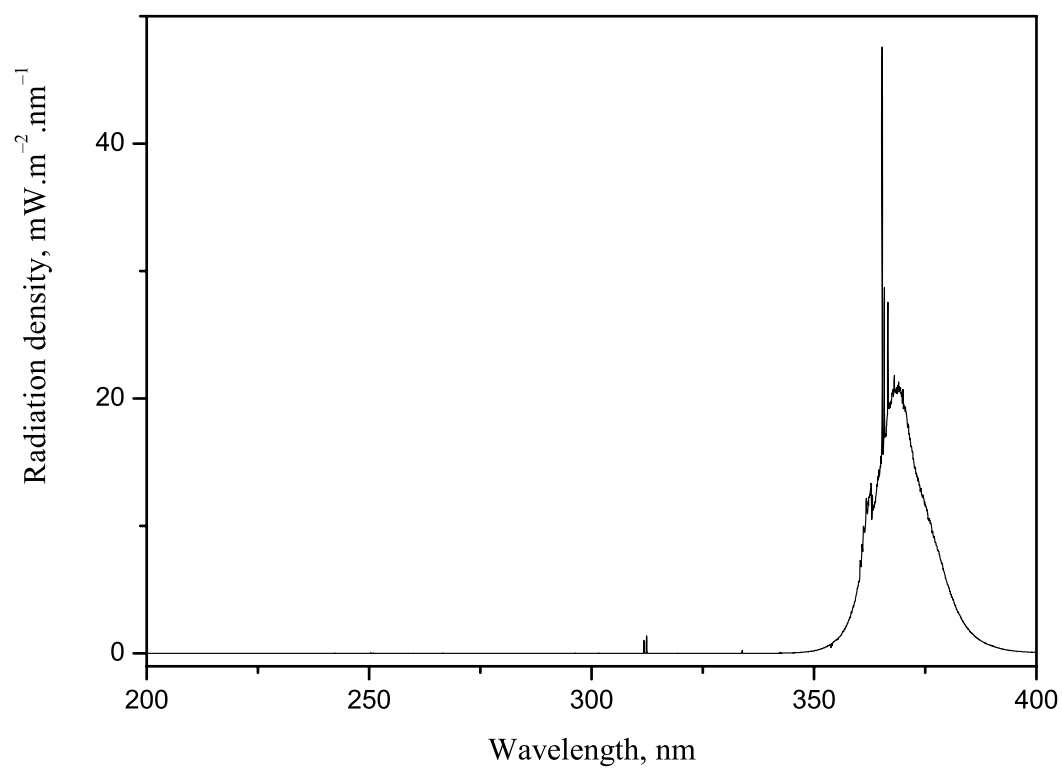


Figure 19 Emission spectrum of the lamp Sylvania Lynx-s 11W BLB

3.2.5 Contact angle measurement

Contact angle (CA) measurement was used as a method for describing wettability (hydrophilicity) of TiO_2 coatings. The used device was Contact Angle System OCA 10, DataPhysics (Figure 20). It requires manual sampling. The device obtains operating elements, which enables to place drops properly on the TiO_2 surface. It also provides drop visualization, due to the CCD camera and SCA software. The contact angle measurement can be taken in various periods of time after the drop is placed on the studied surface. The software enables to evaluate contact angle formed between the tangent of the drop profile and the base line of the surface.



Figure 20 Contact Angle System OCA 10, DataPhysics

The CA was measured on two soda-lime glass plates C and D obtained by piezoelectric deposition. Six drops of a volume of $5\ \mu\text{l}$ each were placed on the plates and the CA was calculated after 10 s after the drop touched the glass surface. The value of CA was calculated as an average of the six measurements for each glass. The same measurement was repeated with irradiated samples C and D under the solar lamp. The irradiation time was 1 minute; the irradiation intensity was $1.5\ \text{mW}\cdot\text{cm}^{-2}$.

4 RESULTS AND DISCUSSION

4.1 Photoinduced hydrophilicity of TiO₂ thin films

Photoinduced hydrophilicity was interpreted by contact angle measurements of water droplets on soda-lime glass plates. The TiO₂ coatings were prepared using TTIP as a template and PEG 1500 (16 g.dm⁻³) as a structure-directing agent. Thin titania layers of 100% relative dot area were obtained by piezoelectric deposition with following calcination. Two, C and D films, were stored in the dark for 10 days; then CA measurements were brought out. The obtained average CA values of the C and D films were lower than 10°. The CA measurement was repeated in the same way after the C and D films were irradiated for 1 minute. The contact angles were not measurable, the average values decreased to zero (Table 2), (Figure 21).

Table 2 Contact angle values of water spread on the TiO₂ coatings prepared by piezoelectric deposition

TiO ₂ film	Contact angle before irradiation (°)	Contact angle after irradiation (°)
C	9.1 ± 0.2	0
D	9.2 ± 0.5	0



Figure 21 Decreasing of the contact angle value of a TiO₂ film without irradiation (left) and after 1 minute irradiation (right)

4.2 Photocatalytic activity of TiO₂ thin films

An indicator ink based on the redox dye 2,6-dichloroindophenol allows the rapid assessment of the activity of thin films. The oxidation reaction of DCIP occurs on the titanium dioxide surface under irradiation of suitable wavelength. Hydroxyl and superoxide radicals formed on the surface can attack molecules of DCIP. In the first step, DCIP undergoes dechlorination reaction followed by oxidation of carbon-structure, resulting in carboxylic acids formation. Carboxylic acids undergo very fast decarboxylation. Photochemical degradation of 2,6-dichloroindophenol can be described by first order kinetics equation.

Photochemical degradation of DCIP was studied on titanium dioxide thin films A and B prepared by piezoelectric deposition on a soda-lime glass plates. Two lamps were used as a source of UV-light.

4.2.1 Calibration curve method

DCIP solutions of known concentrations were prepared to measure their absorption characteristics in the range of wavelength 190–700 nm. It was observed that the absorption maximum corresponds to 600 nm (Figure 22). The calibration curve was obtained as a dependence of maximum absorbance on the molar concentration of the solution. The linear function was calculated as $y = 13790x$ with $R^2 = 0.992$.

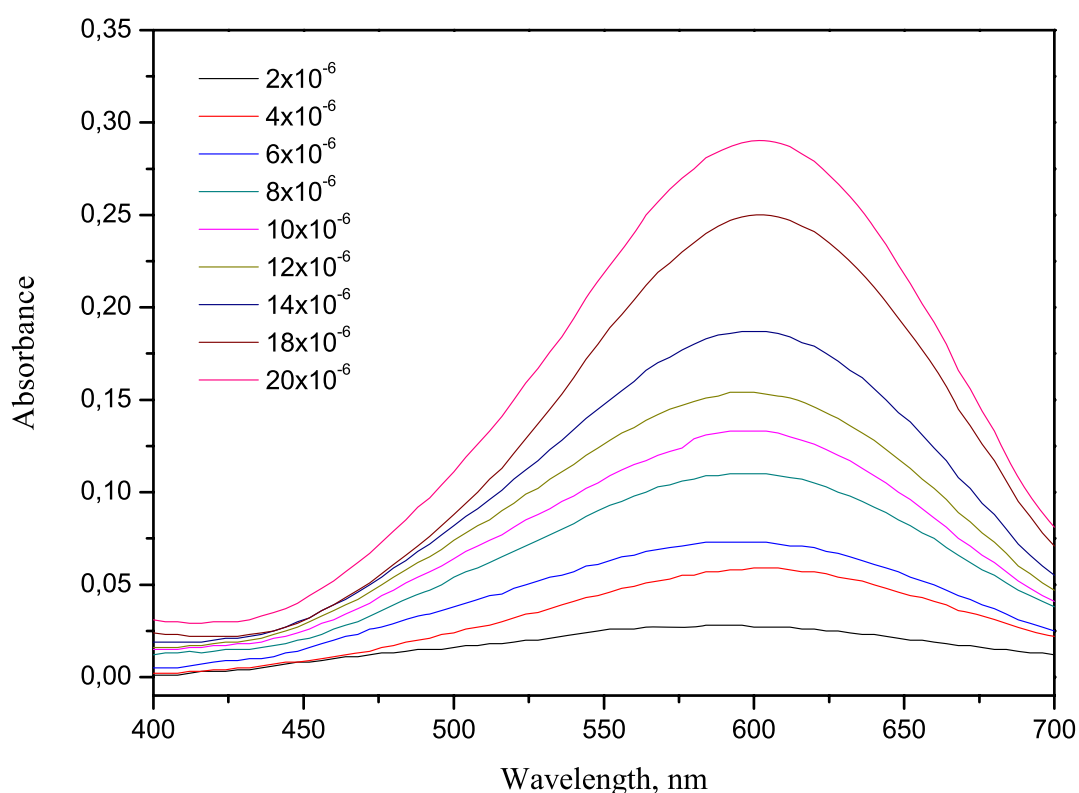


Figure 22 VIS absorption spectrum of 2,6-dichloroindophenol

4.2.2 Photochemical degradation of 2,6-dichloroindophenol

Titanium dioxide thin films A and B were placed into the plate reactor. The intensity of solar lamp irradiation were 4.5 mW.cm^{-2} for the solar lamp and 3 mW.cm^{-2} for the black lamp. DCIP solution was added into the reactor after 15 minute irradiation of the film surface. Absorption curves of DCIP solution samples (3 cm^3) were plotted every 10 minutes. A significant decrease in the absorption peak is observed during the irradiation time. Virgin DCIP solution was used for each degradation reaction.

Formal first rate reaction constant and its standard deviation were estimated using the MS Excel Linregrese function.

Table 3 Rate constant values for photochemical degradation of DCIP for TiO₂ films A and B

Average rate constant k (min ⁻¹)	
Black lamp	0.0009 ± 0.0001
Solar lamp	0.0031 ± 0.0001

The rate constant obtained for the measurements under the solar lamp give higher values than obtained under the black lamp measurement. This could be due to different emission characteristics of both lamps. The solar lamp emits also in the range around 300 nm with higher radiation density compared to the black lamp. The emission character of the solar lamp causes a direct photolysis of DCIP.

5 CONCLUSION

- Transparent titanium dioxide thin films have been prepared through a sol-gel process incorporating PEG 1500 as a structure directing agent and AcAc as a stabilizing agent. Soda-lime glass plates used as a substrate were boiled in sulfuric acid solution to prevent the diffusion of sodium ions to the titania film. Deposited TiO_2 layers were obtained by piezoelectric printing.
- Hydrophilicity of titanium dioxide films were studied using contact angle measurements. CA values obtained on the non-irradiated films and irradiated films under defined conditions were compared. Clear results were obtained indicating a decrease in CA after specified portion of irradiation. The CA values drop from around 10° for non-irradiated films to the zero CA for the irradiated ones.
- Studies on the 2,6-dichloroindophenol sensitivity of the obtained TiO_2 films were performed in this work. Photochemical activity was monitored on films exposed to two different UV-light sources, characterized by different values of irradiation intensities. Degradation of DCIP was analyzed as a decrease of the peak of the absorption curve. This degradation runs according to the first order kinetics, therefore formal first order reaction rate constant could be calculated for both lamps.

6 REFERENCES

- ¹ LITTER, M. I.: Heterogenous photocatalysis. Transition metal ions in photocatalytic systems, *Applied Catalysis B: Enviromental*, 1999, vol. 23, p. 89–114.
- ² BARTHELMY, David. *Mineralogy Database* [online]. 1997-2009 [cit. 2009-05-13]. Dostupný z WWW: <<http://www.webmineral.com/data/Rutile.shtml>>.
- ³ TOMA, Filofteia-Laura, et al. Development of Photocatalytic Active TiO₂ Surfaces by Thermal Spraying of Nanopowders. *Journal of Nanomaterials*. 2008, no. 2008, s. 8.
- ⁴ MILLS, Andrew, et al. A Rapid Method of Assessing the Photocatalytic Activity of Thin TiO₂ Films Using an Ink Based on the Redox Dye 2,6-Dichloroindophenol. *International Journal of Photoenergy*. 2008, no. 2008, s. 6.
- ⁵ MILLS, Andrew , WANG, Jishun , MCGRADY, Mark . Method of Rapid Assessment of Photocatalytic Activities of Self-Cleaning Films. *J. Phys. Chem. B*. 2006, no. 110, s. 18324-18331.
- ⁶ FUJISHIMA, Akira, HASHIMOTO, Kazuhito, WATANABE, Toshiya. *TiO₂ photocatalysis : Fundamentals and Applications*. [s.l.] : [s.n.], 1999. 176 s. ISBN 4-939051-03-X.
- ⁷ LITTER, Marta I. . Heterogeneous photocatalysis Transition metal ions in photocatalytic systems. *Applied Catalysis B: Environmental*. 1999, no. 23, s. 89-114.
- ⁸ *Sol Gel Technology* [online]. 1998 [cit. 2009-05-13]. Dostupný z WWW: <<http://www.chemat.com/html/solgel.html>>.
- ⁹ *UBCerem* [online]. 2005 [cit. 2009-05-13]. Dostupný z WWW: <<http://www.ceramics.mmat.ubc.ca/introduction.html>>.
- ¹⁰ DRBOHLAVOVÁ, J.: Příprava fotokatalyticky aktivních povrchů, Brno, 2008. Disertační práce na Vysokém Učení Technickém v Brně na Ústavu fyzikální a spotřební chemie. Vedoucí diplomové práce Doc. Ing. Michal Veselý, CSc.
- ¹¹ GUO, Bing , et al. Photocatalytic effect of the sol–gel derived nanoporous TiO₂ transparent thin films. *Thin Solid Films*. 2005, no. 479, s. 310-315.
- ¹² NARAYANASWAMY, Arun , et al. Synthesis and characterization of porous TiO₂ with wormhole-like framework structure. *J Porous Mater*. 2008, no. 15, s. 21-27.
- ¹³ YU, Jiaguo , ZHAO, Xiujian . Effect of surface treatment on the photocatalytic activity and hydrophilic property of the sol-gel derived TiO₂ thin films. In *Materials Research Bulletin*. [s.l.] : [s.n.], 2000. s. 97-107.

- ¹⁴ KUZNETSOVAA, I.N. , BLASKOV , V., ZNAIDI, L. . Study on the influence of heat treatment on the crystallographic phases of nanostructured TiO₂ films. *Materials Science and Engineering B*. 2007, no. 137, s. 31-39.
- ¹⁵ ARCONADA, N. , et al. Synthesis and photocatalytic properties of dense and porous TiO₂-anatase thin films prepared by sol–gel. *Applied Catalysis B: Environmental*. 2008, no. in press, s. 7.
- ¹⁶ ARPI, Majumder, et al. Study of gradual variation of structural, surface morphological and photocatalytic properties of sol-gel derived transparent TiO₂ thin film. *Journal of Physics: Conference Series*. 2008, no. 100, s. 4.
- ¹⁷ HAKOLA, Liisa . Inkjet Printing For Making Fine Conductors and Multi Layer Electronics. In *UV & EB Technology Expo & Conference*. [s.l.] : [s.n.], 2006. s. 19. Dostupný z WWW: <http://www.vtt.fi/inf/julkaisut/muut/2006/RT2006_Hakola.pdf>.
- ¹⁸ VEILLET, Ray . *PicoJet | Technology - Drop-on-Demand IJ Printing* [online]. 2008 [cit. 2009-05-13]. Dostupný z WWW: <<http://www.picojet.com/drop-on-demand.asp>>.
- ¹⁹ LE, Hue P. . Progress and Trends in Ink-jet Printing Technology. *Journal of Imaging Science and Technology* [online]. 1998, no. 42 [cit. 2009-05-13]. Dostupný z WWW: <<http://www.imaging.org/resources/leinkjet/part2.cfm>>.
- ²⁰ *HowStuffWorks "How Inkjet Printers Work"* [online]. 1998-2009 [cit. 2009-05-13]. Dostupný z WWW: <<http://computer.howstuffworks.com/inkjet-printer3.htm>>.
- ²¹ [38] Michal Veselý, Petr Dzik, Mária Veselá, Jana Chomoucká: Printed layers of titanium dioxide, 2nd Czech-Austrian Workshop Telč, 2008.
- ²² WATANABE, Toshiya, et al. Photocatalytic Activity and Photo-Induced Wettability Conversion of TiO₂ Thin Film Prepared by Sol-Gel Process on a Soda-Lime Glass. *Journal of Sol-Gel Science and Technology*. 2000, no. 19, s. 71-76.
- ²³ BARTOVSKÁ Lidmila: *Chemická kinetika* [online]. Version 1.0. Praha : VŠCHT Praha, 2008 [cit. 2009-05-13]. Available from www: <http://vydavatelstvi.vscht.cz/knihy/uid_isbn-978-80-7080-670-8/pages-img/obalka-1.html>. ISBN 978-80-7080-670-8.
- ²⁴ KUMAR, K. Vasanth, PORKODI, K. , ROCHA, F. Langmuir–Hinshelwood kinetics – A theoretical study. *Catalysis Communications*. 2009, no. 9, s. 82-84.
- ²⁵ LUND, Carl. *Su28_reading.pdf (application/pdf objekt)* [online]. 2005 [cit. 2009-05-13]. Dostupný z WWW: <http://www.eng.buffalo.edu/Courses/obsolete/ce429/study_units/readings/su28_reading.pdf>.

- ²⁶ CHOMOUCKÁ, J.: *Příprava samočisticích fotokatalyticky aktivních vrstev*, Brno, 2005. Diplomová práce na Vysokém Učení Technickém v Brně na Ústavu fyzikální a spotřební chemie. Vedoucí diplomové práce Doc. Ing. Michal Veselý, CSc.
- ²⁷ *KSV Instruments Ltd: Contact Angle* [online]. 2009 [cit. 2009-05-13]. Dostupný z WWW: <<http://www.ksvltd.com/content/index/keyca>>.
- ²⁸ KIPPHAN, H. *Handbook of print media*. [s.l.] : [s.n.], 2000. ISBN 3-540-67326-1. Fundamentals, s. 90-99.
- ²⁹ PANÁK, Ján, et al. *Polygrafické minimum*. [s.l.] : [s.n.], 2000. 264 s. ISBN 80-967811-3-8.

7 LIST OF ABBREVIATIONS

HP	Heterogeneous Photocatalysis
SC	Semiconductor
VB	Valence band
CB	Conduction band
SDR	Structural Directing Reagent
CS	Continual stream
DOD	Drop-on-Demand
DCIP	2,6-dichloroindophenol
TTIP	Titanium(IV)isopropoxide
PEG	Polyethylene glycol
CA	Contact angle